



Australian Government

PCT/AU2004/000462

REC'D 06 MAY 2004

WIPO

PCT

Patent Office
Canberra

I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003901735 for a patent by UNISEARCH LIMITED as filed on 11 April 2003.

BEST AVAILABLE COPY

WITNESS my hand this
Twenty-third day of April 2004

6

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant(s):

UNISEARCH LIMITED

Invention Title:

DURABLE SUPERHYDROPHOBIC COATING

The invention is described in the following statement:

DURABLE SUPERHYDROPHOBIC COATING

Technical Field

5 This invention relates to the technology of coatings. In particular, the invention relates to a method for forming superhydrophobic coatings on the surface of a substrate, and superhydrophobic coatings prepared by the method.

Background to the Invention

10 Wettability is an indicator of the affinity of a solid surface for a liquid. The wettability of a surface is dependent on both the physical and chemical heterogeneity of the surface.

The contact angle θ made by a droplet of liquid on the surface of a solid substrate has been used as a quantitative measure of the wettability of the surface. If the liquid
15 spreads completely across the surface and forms a film, the contact angle θ is 0° . If there is any degree of beading of the liquid on the surface, the surface is considered to be non-wetting.

A surface is usually considered to be hydrophobic if the contact angle of a droplet of water is greater than 90° . Coatings on which water has a contact angle greater than 90°
20 are referred to as hydrophobic coatings. Surfaces with water contact angles greater than 130° are commonly referred to as superhydrophobic. Similarly, coatings on which water has a contact angle greater than 130° are commonly referred to as superhydrophobic coatings.

25 Hydrophobic surfaces have little or no tendency to absorb water and water forms a discrete droplet on the surface. An example of a hydrophobic surface is a polytetrafluoroethylene (TeflonTM) surface. Water contact angles on a polytetrafluoroethylene surface can reach about 115° . This is about the upper limit of
30 hydrophobicity on smooth surfaces. The contact angle of a droplet of water on a surface can be increased, however, by causing the surface to become physically roughened.

If the surface is rough or heterogeneous there are usually two contact angles that can be measured. Tilting the surface until the droplet is about to roll off illustrates this
35 phenomena. The contact angle of the leading edge of the droplet represents the largest measurable contact angle and is called the advancing contact angle or θ_{adv} . The contact angle of the receding edge of the droplet represents the minimum measurable contact

angle and is called the receding contact angle or θ_{rec} . The difference between the advancing and receding contact angles is known as the contact angle hysteresis and defines the degree of dynamic wettability.

- 5 The contact angle hysteresis of water indicates the stability of a droplet of water on the surface, the lower the contact angle hysteresis the less stable the droplet is and therefore the easier the water droplet slides off the surface.

Hydrophobic coatings, and in particular superhydrophobic coatings, have many uses.

- 10 Hydrophobic coatings are used to render surfaces water proof or water resistant. Superhydrophobic coatings have a "self-cleaning" property as dirt, bacteria, spores or other substances which come into contact with the surface cannot readily adhere to the coating and are readily washed off by water. Such coating are therefore used to render surfaces resistant to attachment by water soluble electrolytes, such as acids and alkalies, and by dirt and micro-organisms. Such coatings are also used to render surfaces resistant to icing and fouling.

Methods of forming superhydrophobic coatings, and applying superhydrophobic coatings to surfaces, have been described in the prior art. For example, WO 98/42452 and WO 01/14497 describe methods of forming superhydrophobic coatings. However, the superhydrophobic coatings formed by the methods described in WO 98/42452 and WO 01/14497 are generally easily damaged and removed from the surface to which they are applied. Such coatings therefore have a limited lifespan when exposed to an abrasive environment.

- 25 In view of the many practical uses of superhydrophobic coatings, it would be advantageous to develop methods of preparing more durable superhydrophobic coatings.

30 Summary of the Invention

In a first aspect, the present invention provides a method of forming a hydrophobic coating on the surface of a substrate, the method comprising the steps of:

- (a) applying a mixture comprising a particulate material and a linking agent to the surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material;

- (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands, and
- (c) exposing the coating to conditions effective to cause at least some of the polymer strands linking two or more particles or linking the surface and one or more particles, to cross-link with other polymer strands linking two or more particles or linking the surface and or one more particles,
- thereby forming a hydrophobic coating on the surface on which water has a contact angle of at least 130° .

Preferably, the hydrophobic coating is such that the contact angle of water on the coating is at least 150° , more preferably at least 160° , and even more preferably, at least 165° .

In the hydrophobic coatings produced by the method of the present invention, the particles of the particulate material are linked together and to the surface by polymer strands, and at least some of the polymer strands are cross-linked, thereby forming a three-dimensional network of cross-linked polymer strands which results in a more durable hydrophobic coating than the coatings prepared by the methods described in WO 98/42452 or WO 01/14497.

The polymer strands may be cross-linked by any means known in the art for cross-linking polymers. Preferred means are by a radical cross-linking reaction catalysed by peroxide or by a vinyl addition cross-linking reaction catalysed by a platinum catalyst. In some embodiments of the invention, the mixture comprising the particulate material and the linking agent further comprises a polymer having terminal vinyl groups and a platinum catalyst to catalyse a vinyl cross-linking reaction between the polymer having terminal vinyl groups and the polymer strands formed by the linking agent. The polymer having terminal vinyl groups may, for example, be selected from vinyl terminated polydimethylsiloxane, vinyl terminated diphenylsiloxane-dimethylsiloxane copolymer, vinyl terminated trifluoropropylmethylsiloxane-dimethylsiloxane copolymer and vinylmethyloxysiloxane homopolymer. The polymer strands may also be cross-linked by dehydrogenative coupling in which a hydrosilane group on one polymer strand reacts with a silanol group on another polymer strand.

Accordingly, in one embodiment, the present invention provides a method of forming a hydrophobic coating on the surface of a substrate, the method comprising the steps of:

- 5 (a) applying a mixture comprising a particulate material, a linking agent and a peroxide, to the surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material, and wherein the peroxide is capable of causing a peroxide catalysed cross-linking reaction between the polymer strands formed by the linking agent;
- 10 (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands, and
- 15 (c) exposing the coating to conditions effective to cause a peroxide catalysed cross-linking reaction between at least some of the polymer strands linking two or more particles or linking the surface and one or more particles, thereby forming a hydrophobic coating on the surface on which water has a contact angle of at least 130°.

20 In another embodiment, the present invention provides a method of forming a hydrophobic coating on the surface of a substrate, the method comprising the steps of:

- 25 (a) applying a mixture comprising a particulate material, a linking agent and a platinum catalyst, to the surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material, and wherein the platinum catalyst is capable of catalysing a cross-linking reaction between the polymer strands formed by the linking agent;
- 30 (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands, and
- 35 (c) exposing the coating to conditions effective to cause a platinum catalysed cross-linking reaction between at least some of the polymer strands linking two or more particles or linking the surface and one or more particles,

thereby forming a hydrophobic coating on the surface on which water has a contact angle of at least 130° .

In another embodiment, the present invention provides a method of forming a

- 5 hydrophobic coating on the surface of a substrate, the method comprising the steps of:
- (a) 10 applying a mixture comprising a particulate material, a linking agent, a polymer having terminal vinyl groups and a platinum catalyst, to the surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material, and wherein the platinum catalyst is capable of catalysing a vinyl addition cross-linking reaction between the polymer having terminated vinyl groups and the polymer strands formed by the linking agent;
 - 15 (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands, and
 - 20 (c) exposing the coating to conditions effective to cause a vinyl addition cross-linking reaction between the polymer having terminal vinyl groups and the polymer strands linking two or more particles or linking the surface and one or more particles,

thereby forming a hydrophobic coating on the surface on which water has a contact angle of at least 130° .

In a second aspect, the present invention provides a hydrophobic coating formed by the method according to the first aspect of the present invention.

- 30 In a third aspect, the present invention provides an object having a surface at least a portion of which is coated with a hydrophobic coating formed by the method according to the first aspect of the present invention.

Detailed Description of the Invention

35

Particulate Material

The particulate material may consist of particles having substantially equal diameters,

or alternatively particles having a spectrum of diameters. Preferably, at least some of the particles have diameters within the range of from 1 nm to 500 μm . More preferably, all or substantially all of the particles have diameters in the range of from 1 nm to 500 μm , more preferably, in the range from 1 nm to 100 μm , still more preferably, in the range of from 1 nm to 1 μm , still more preferably, in the range of from 1 nm to 100 nm, and even more preferably in the range of from 5 nm to 50 nm.

In one embodiment, the particulate material consists of particles having an average particle size (diameter) in the range of from 1 nm to 500 μm . In a further embodiment, the average particle size is in the range of from 5 nm to 50 nm. In yet a further embodiment, the average particle size is in the range of from 5 nm to 20 nm. In yet a further embodiment, the average particle size is about 15 nm.

In a preferred embodiment of the invention, the particulate material consists of silica particles, such as flame-hydrolysed silica particles. However, other particulate material comprising particles of an appropriate size could be used. Other particulate materials which could be used include metal particles, glass particles and particles of metal oxides, such as titanium oxide, aluminium oxide, zirconium oxide and zinc oxide.

The particulate material may comprise a mixture of two or more types of particles. For example, the particulate material may comprise a mixture of silica particles and particles of a metal oxide.

Chemical Modifying Reagent

In some embodiments, the particles of the particulate material are modified by contact with a chemical modifying reagent capable of reacting with the particles to enhance the chemical hydrophobicity of the particles, and thus the coating formed by the method of the present invention.

Typically, the chemical hydrophobicity of the particles is enhanced by the chemical modifying reagent reacting with a hydrophilic group on the surface of the particles to remove the hydrophilic group or to convert the hydrophilic group to a hydrophobic group. The chemical modifying reagent may also react with the surface of the particles to form functional groups on the surface of the particles to facilitate binding of the particles to the linking agent in step (b) of the method of the present invention.

The particulate material may be contacted with the chemical modifying reagent prior to

formation of the mixture comprising the particulate material and the linking agent. Alternatively, the chemical modifying reagent may be included in the mixture comprising the particulate material and the linking agent applied to the surface in step (a) of the method of the present invention. Accordingly, in some embodiments of the present invention, the mixture applied to the surface in step (a) further comprises a chemical modifying reagent capable of reacting with at least some of the particles of the particulate material to enhance the chemical hydrophobicity of the particles.

In some embodiments of the present invention, the chemical modifying reagent also enhances the cross-linking of the polymer strands by binding to the polymer strands and providing additional cross-linking sites.

The chemical modifying reagent may be a compound containing one or more condensation cure groups and one or more hydrophobic groups. The one or more condensation cure groups may include one or more of the following groups: acetoxyl, enoxy, oxime, alkoxyl, or amine. Such chemical modifying reagents include compounds of the formula $\text{SiR}(\text{OAc})_3$, where R is a hydrophobic group such as methyl, ethyl, vinyl or trifluoropropyl, and Ac is an acetyl group.

The same compound may act as both a linking agent and a chemical modifying reagent. Alternatively, different compounds may be used as the linking agent and the chemical modifying reagent.

Linking Agent

The linking agent may be any compound or mixture of compounds capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming polymer strand linking the surface and one or more particles of the particulate material.

In some embodiments, the linking agent is a polymer or mixture of polymers capable of covalently binding to two or more particles of the particulate material thereby linking the particles by a polymer strand, and capable of covalently binding to the surface and one or more particles of the particulate material thereby linking the surface and the one or more particles by a polymer strand.

When the particles of the particulate material have hydroxyl groups on the surface of the particles, suitable polymers include siloxane polymers. Such polymers are capable

of binding to hydroxyl groups on the surface of the particles via a condensation reaction. This reaction can also render the surface of the particle chemically hydrophobic. For example, when the particulate material is flame-hydrolysed silica particles, the siloxane polymers are capable of binding to hydroxyl groups on the surface of the silica particles, thereby changing the hydrophilic silanol group ($\equiv\text{Si-OH}$) to a hydrophobic siloxane group ($\equiv\text{Si-O-Si}\equiv$).

Suitable siloxane polymers include hydroxy terminated vinylsiloxane polymer, hydroxy terminated polydimethylsiloxane (PDMS), hydroxy terminated polydiphenylsiloxane, hydroxy terminated polyphenylmethylsiloxane, methylhydrosiloxane (and copolymers with dimethylsiloxane), vinylmethoxysiloxane homopolymer, polytrifluoropropylmethylsiloxane (silanol terminated), vinylmethylsiloxane-dimethylsiloxane copolymer (silanol terminated) and vinylmethylsiloxanes.

The invention is not limited, however, to methods involving the use of siloxane polymers. Other polymers that can be used which do not contain silica include modified polystyrene, polyethylenes and fluorinated polymers. Suitable polymers also include triethoxysilyl modified poly-1,2-butadiene and polyethylene-co-trialkoxysilane.

In some embodiments of the present invention, the linking agent is a monomer or mixture of monomers capable of forming a polymer strand linking two or more particles of the particulate material, and capable of forming a polymer strand linking the surface and one or more particles of the particulate material. Such a linking agent links the two or more particles by a polymer strand covalently bound to the particles, and links the surface and one or more particles by a polymer strand covalently bound to the surface and the one or more particles. Such linking agents may for example, be selected from methyltrimethoxysilane, vinyltrimethylsilane, methyltris(methylethylketoximino)silane, methyltriacetoxysilane, ethyltriacetoxysilane and vinyltriacetoxysilane. When such a linking agent is used, the mixture comprising the particulate material and the linking agent typically further comprises water (for hydrolysis) and a catalyst to catalyse polymerisation of the monomer.

Mixture

The mixture comprising the particulate material and the linking agent may include other components.

For example, the mixture may include a chemical modifying reagent as described

above. The mixture will typically also include a solvent, preferably an organic solvent, for example, hexane, ethyl acetate, toluene, methylethyl ketone or diethyl ether.

5 The mixture may also include components for catalysing the cross-linking of the polymer strands formed by the linking agent. For example, the mixture may include a peroxide for cross-linking the polymer strands by a peroxide catalysed reaction. Similarly, the mixture may include a platinum catalyst for catalysing the cross-linking of the polymer strands by a vinyl addition reaction.

10 In some embodiments of the invention, polymers which do not have groups that enable them to bind to the particles of the particulate material may be included in the mixture at step (a). For example, polymers having terminal vinyl groups which are not capable of binding to the particles of the particulate material or the surface, but which can bind to other polymers via cross-linking reactions, may be included in the mixture to
15 facilitate cross-linking between the polymer strands.

In step (a) of the method of the present invention, the mixture may be applied to the surface of the substrate by separately applying the components of the mixture to the surface and mixing the components on the surface. However, more typically, the
20 mixture comprising the particulate material and the linking agent is first prepared and the mixture then applied to the surface.

The mixture comprising the particulate material and the linking agent may be prepared by mixing the particulate material, the linking agent, and the other components of the
25 mixture, if any, in an ultrasonic bath.

The mixture is typically applied to the surface as a slurry. This can be achieved by including one or more solvents, preferably organic solvents, in the mixture. One solvent found to be particularly suitable when the particulate material comprises silica particles
30 is hexane, however, other solvents could be used, for example diethyl ether.

The mixture may be applied to the surface by any technique suitable for forming a coating on a surface of a substrate. One technique is to paint the mixture onto the surface. A second technique is dip coating. In this technique, the substrate is immersed
35 in the mixture and withdrawn at a particular rate. A third technique is spin coating. In this technique, the substrate is attached to a horizontal platform capable of spinning at a high rate, such as a few thousand rpm. The mixture is deposited drop-wise onto the

substrate whilst it is spinning, which results in a highly uniform coating on the surface of the substrate. The coating thickness can be controlled by adjusting the spin rate or the volume of mixture deposited. A further coating technique is spray coating. In this technique, a spray solution of the mixture is sprayed onto the surface of the substrate at an appropriate distance, flow rate and length of time such that a uniform coating of adequate thickness is formed.

In some embodiments of the present invention, after the mixture has been applied to the surface, the mixture may be treated to remove solvent(s) from the mixture. This treatment may include heating the applied mixture to a temperature which causes the solvent(s) to evaporate, but which does not exceed the melting point of the substrate or any components of the mixture (other than the solvent(s)), or exceed the temperature at which the substrate or any of the components of the mixture (other than the solvent(s)) decomposes. The drying time will depend on a number of factors such as the thickness of the mixture applied to the surface and the components of the mixture.

Vacuum drying, or a combination of vacuum drying and heating, may be preferable if the substrate has a low melting point.

20 Steps (b) and (c)

Step (b) of the method of the invention involves exposing the coating to conditions under which the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands. The conditions will vary depending on the particulate material and the linking agent used. The appropriate conditions can be readily determined by a person skilled in the art.

In some embodiments of the invention, the linking agent may form polymer strands linking two or more particles of the particulate material, and form polymer strands linking the surface and one or more particles of the particulate material, at ambient temperatures (for example at about 15 to 25°C). In such a case, step (b) may involve exposing the coating to ambient temperatures for a time sufficient for the linking agent to form polymer strands linking two or more particles of the particulate material, and polymer strands linking the surface and one or more particles of the particulate material.

When a monomer such as methyltriacetoxysilane is used as the linking agent, step (b)

typically involves heating the coating to a temperature and for a time effective for the linking agent to form polymer strands linking two or more particles of the particulate material, and form polymer strands linking the surface and one or more particles of the particulate material.

5

Step (c) of the method of the present invention involves exposing the coating to conditions effective to cause at least some of the polymer strands linking two or more particles of the particulate material or linking the surface and one or more particles of the particulate material, to cross-link with other polymer strands linking two or more particles or linking the surface and one or more particles.

10

The polymer strands may be cross-linked by any means known in the art for cross-linking polymers. Preferred means are by a radical cross-linking reaction catalysed by peroxide or by a vinyl addition cross-linking reaction catalysed by a platinum catalyst. In some embodiments of the invention, the mixture comprising the particulate material and the linking agent further comprises a polymer having terminal vinyl groups and a platinum catalyst to catalyse a vinyl cross-linking reaction between polymer having terminal vinyl groups and the polymer strands. The polymer strands may also be cross-linked by dehydrogenative coupling, in which a hydrosilane group on one polymer strand reacts with a silanol group on another polymer strand.

15

20

The conditions of step (c) of the method of the present invention will vary depending on the particulate material and the linking agent used and the reaction used to cross-link the polymer strands. The appropriate conditions can be readily determined by a person skilled in the art.

25

As mentioned above, in some embodiments of the present invention, the polymer strands are cross-linked by a radical cross-linking reaction catalysed by peroxide. The radical cross-linking reaction catalysed by peroxide typically involves the radical addition of a vinyl group with a methyl or methylene group to form a covalent bond. The reaction may be between a vinyl group on one polymer strand and a methyl or methylene group on an adjacent polymer strand. Alternatively, the reaction may be between such groups on a polymer strand and an adjacent chemical modifying reagent, with concomitant or subsequent reactions with another polymer strand or chemical modifying reagent or reagents forming a cross-link with another polymer strand. This reaction occurs in the temperature range of about 100 to about 150 °C in a time of about 10 to about 180 minutes. Accordingly, in these embodiments of the present invention,

30

35

step (c) typically involves heating the coating to a temperature of from about 100 °C to about 150 °C for a time effective to cause at least some of the polymer strands to cross-link. In some cases, a cross-linking reaction may occur even if no vinyl groups are present, provided a large amount of peroxide is used. The peroxide may be any
5 peroxide capable of catalysing the cross-linking reaction, for example, dicumyl peroxide, 2,4-dichlorobenzoyl peroxide, or benzoyl peroxide.

In some embodiments of the present invention, the polymer strands are cross-linked by a vinyl addition cross-linking reaction in the presence of a platinum catalyst to catalyse
10 the reaction. The reaction may be between a vinyl group on one polymer strand and a hydrosilane group on an adjacent polymer strand. Alternatively, the reaction may be between such groups on a polymer strand and an adjacent chemical modifying reagent, with concomitant or subsequent reactions with another polymer strand or chemical
15 modifying reagent or reagents forming a cross-link with another polymer strand. Suitable platinum catalysts include platinum divinyl complexes or platinum cyclovinyl complexes. Such reactions can be carried out at room temperatures or heat cured at up to about 150°C. Accordingly, in these embodiments of the invention, step (c) typically involves exposing the coating to ambient temperatures or heating the coating up to about 150°C.

20 In some embodiments of the present invention, step (b) is carried out prior to step (c). In other embodiments of the present invention, steps (b) and (c) are carried out simultaneously.

25 The hydrophobicity of the coatings formed by the method of the present invention is due to a combination of both the intrinsic chemical hydrophobicity of the surface of the coating and the physical surface structure of the surface of the coating. Accordingly, during the method of the present invention, the particles of the particulate material, if not initially chemically hydrophobic, typically become chemically hydrophobic. The
30 particles of the particulate material may become chemically hydrophobic as a result of the particles reacting with the linking group, or reacting with a chemical modifying reagent. Similarly, it is preferred that the linking agent forms polymer strands which are chemically hydrophobic.

35 In order that the present invention may be more clearly understood, the invention will now be described with reference to certain preferred embodiments.

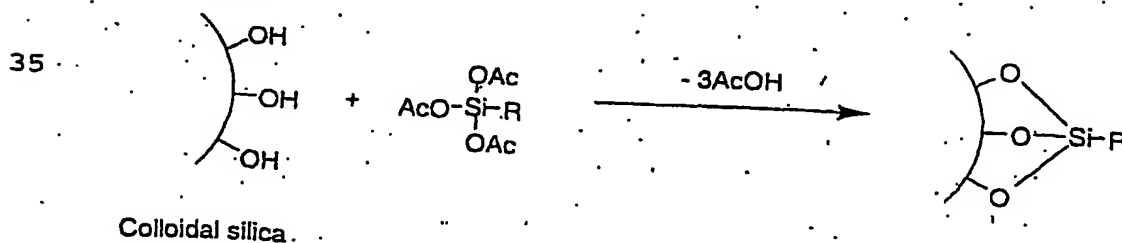
In a preferred embodiment, the particulate material is silica particles and the linking agent is a siloxane polymer, such as hydroxy terminated PDMS, or a monomer such as methyltriacetoxysilane. Suitable silica particles include commercially available flame-hydrolysed silica powder, available as Aerosil™ silica powder from Degussa Limited with particles having a primary size in the range of 5 to 50 nm. Flame-hydrolysed silica particles are hydrophilic, as the surface of the particles contains the hydrophilic silanol functional group ($\equiv\text{Si-OH}$). However, the surface chemistry of the particles is changed during the method of the invention, as the silanol functional groups ($\equiv\text{Si-OH}$) are converted to the hydrophobic siloxane functional groups ($\equiv\text{Si-O-Si}\equiv$) through reactions with the linking agent or a chemical modifying reagent.

It is preferred to modify the silica particles with a chemical modifying reagent such as a compound of the formula $\text{SiR}(\text{OAc})_3$, where R is a hydrophobic group such as an alkyl group (e.g. methyl or ethyl), vinyl or trifluoropropyl, and Ac is an acetyl group, by including the chemical modifying reagent in the mixture comprising the particulate material and the linking agent applied to the surface in step (a) of the method of the present invention.

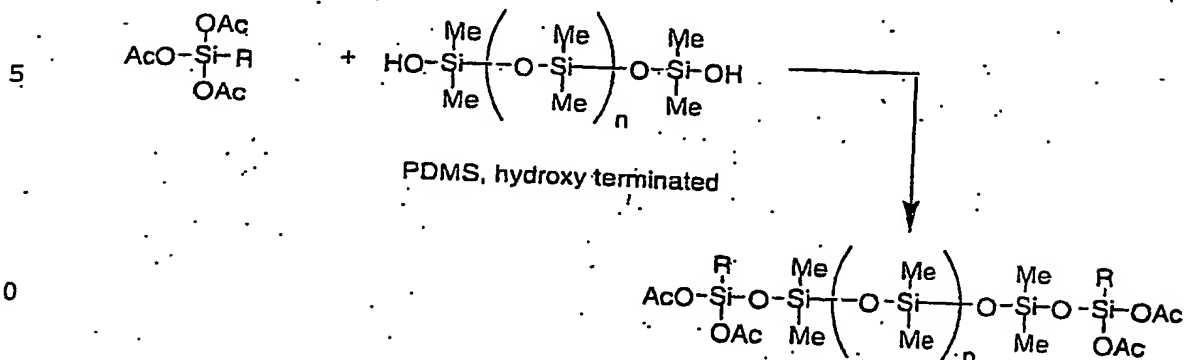
Hydroxy terminated PDMS is a preferred linking agent because it is unusually resistant to heat, being able to withstand temperatures up to about 400°C without deformation. It also has high electrical resistance, and is able to withstand outdoor exposure to UV radiation with little or no deformation or degradation for at least 10 years. PDMS is terminated with hydroxyl groups which function as sites where the PDMS molecules are able to react with and bond to two silica particles. The PDMS becomes chemically hydrophobic when the hydroxyl groups are removed by reaction with the silica particles.

In such preferred embodiments of the present invention, the primary reactions which occur between the silica particles, the linking agent such as PDMS, and the chemical modifying reagent are set out below:

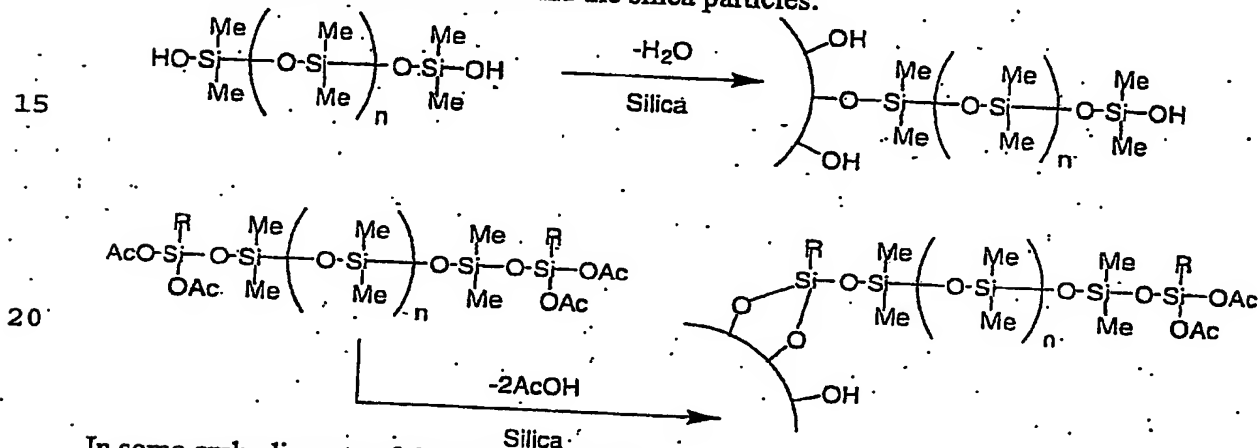
1) condensation reaction between the silica particles and the chemical modifying reagent:



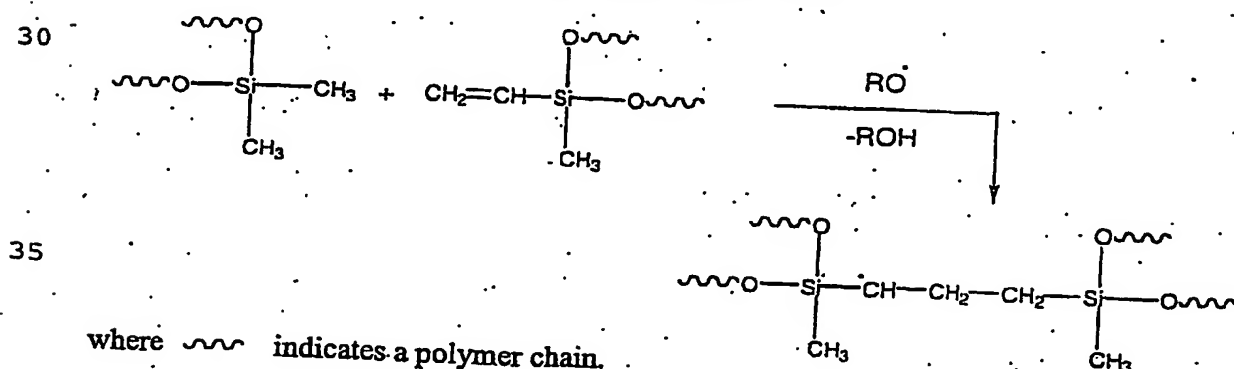
- 2) reaction between PDMS and the chemical modifying reagent:



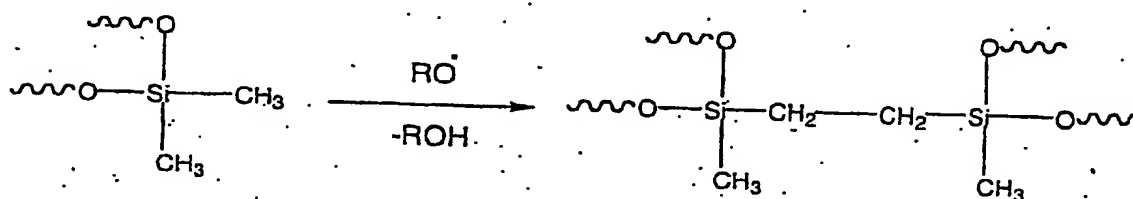
- 3) reaction between PDMS and the silica particles:



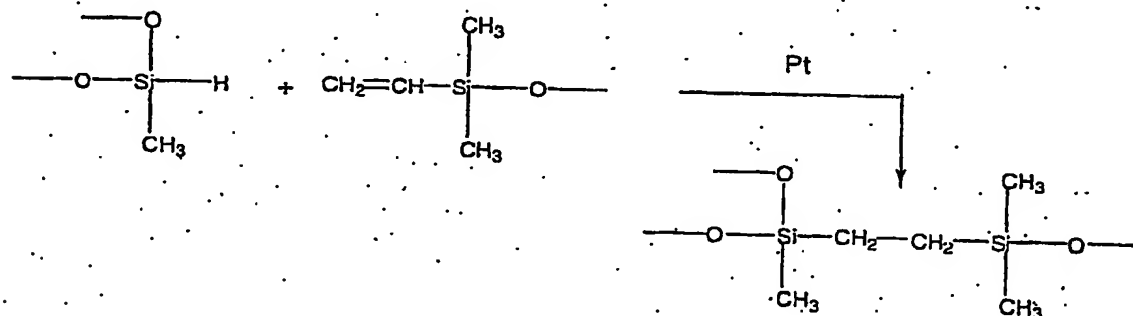
In some embodiments of the present invention, the polymer strands formed by the linking agent contain vinyl groups. Such polymer strands can be cross-linked via peroxide induced radical cross-linking reactions between vinyl and methyl groups on adjacent polymer strands. Concomitant and subsequent reactions take place among methyl groups and between cross-link sites and methyl groups. The initial cross-linking reaction for vinylmethylsiloxane copolymers is as follows:



A cross-linking reaction may occur even if no polymer strands have vinyl groups, provided a large amount of peroxide is present. In such a case, the reaction which causes cross-linking is as follows:



In some embodiments of the invention, polymers having terminal vinyl groups are included in the mixture of the particulate material and the linking agent. In such a case, the polymer strands may be cross-linked via a vinyl addition cross-linking reaction, using a platinum complex as a catalyst. The reaction scheme is as follows:



Examples

In the following examples, the particulate material is flame-hydrolysed silica powder having a primary particle size of 5 to 50 nm. The flame-hydrolysed silica powder used was AerosilTM silica. The specific surface area of AerosilTM silica is about 50-600 m²/g. The large specific surface area represents an important characteristic of AerosilTM silica. Since the specific surface area of the AerosilTM silica is large in relation to the mass, the surface chemistry plays a significant role and influences the surface properties of the coating formed using such particles.

Comparative Example

A hydrophobic coating was applied to the surface of a glass substrate and a rubber substrate as described below.

- The following were mixed together:

0.4g PDMS (hydroxy terminated)

CAS [70131-67-8]

0.3g methyltriacetoxysilane

CAS [4253-34-3]

0.1g Aerosil silica powder, and

~ 20 ml hexane.

- The mixture was mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes to disperse the particles and form a uniform mixture. Vibration frequencies of about 40 kHz were used.

- The mixture was removed from the ultrasonic bath.

- Without allowing the mixture to settle, the mixture was deposited onto the surface of the substrate by spray coating. Other techniques such as spin coating or dip coating could have been used.

- The coated substrate was placed in an oven at a temperature of about 150°C for 10 to 30 minutes. The coated substrate could alternatively have been cured at room temperature.

The contact angle and hysteresis of water on the coated surfaces were measured by an automated contact angle instrument goniometer (made by Ramé-hart, Inc) to be:

Glass substrate

Contact angle: 154°

Hysteresis: 75°

Rubber substrate

Contact angle: 155°

Hysteresis: 31°

Example 1

In this example, a hydrophobic coating was applied to the surface of a glass and rubber substrate using a method similar to that in the above Comparative Example, except that the polymer strands formed by the linking agent (hydroxy terminated PDMS) were cross-linked via a free radical cross-linking reaction. The cross-linking reaction was catalysed by the presence of a large amount of peroxide.

The coatings were applied as follows:

- The following were mixed together

0.4g PDMS (hydroxy terminated)

CAS [70131-67-8]

0.3g methyltriacetoxysilane

CAS [4253-34-3]

0.1g dicumyl peroxide

CAS [80-43-3]

5 0.1g Aerosil silica powder, and
~ 20 ml hexane

- The mixture was mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes to disperse the particles and form a uniform mixture. Vibration frequencies of about 40 kHz were used.

- 10 • The mixture was removed from the ultrasonic bath.

- Without allowing the mixture to settle, drops of the mixture were deposited on the surface of the substrate by spray coating.

- The coated substrate was placed in oven at a temperature of about 150°C for 30-60 minutes.

15 The contact angle and hysteresis of water on the coated surfaces were measured by an automated contact angle instrument goniometer (made by Ramé-hart, Inc) to be:

Glass

20 Contact angle: 166°

Hysteresis: 19°

Rubber

Contact angle: 166°

25 Hysteresis: 55°

Example 2:

In this example, a hydrophobic coating was applied to the surface of a glass substrate and a rubber substrate as described below. In this example, the linking agent was
30 vinylsiloxane polymer (hydroxy terminated). This polymer includes vinyl groups which are able to react with methyl groups of adjacent polymers. The polymer strands formed by this linking agent were cross-linked via a free radical cross-linking reaction using a catalytic amount of peroxide.

- 35 • The following were mixed together

0.50g vinylsiloxane polymer (hydroxy terminated)

CAS [67923-19-7]

0.36g methyltriacetoxysilane

CAS [4253-34-3]

0.03g dicumyl peroxide

CAS [80-43-3]

0.12g Aerosil silica powder, and

~ 25 ml hexane

- 5 • The mixture was mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes to disperse the particles and form a uniform mixture. Vibration frequencies of about 40 kHz were used.
- The mixture was removed from the ultrasonic bath.
- Without allowing the mixture to settle, drops of the mixture were deposited onto the surface of the substrate by spray coating.
- 10 • The coated substrate was placed in oven at a temperature of about 150°C for 30-60 minutes. The coated substrate alternatively could have been cured at room temperature if desired.

15 The contact angle and hysteresis on the coated surfaces were measured by an automated contact angle instrument goniometer (made by Ramé-hart, Inc) to be:

Glass

Contact angle: 166°

Hysteresis: 9°

20

Rubber

Contact angle: 162°

Hysteresis: 35°

25 **Example 3**

In this example, a hydrophobic coating was applied to the surface of a glass substrate and a rubber substrate as described below. The mixture applied to the surface of the substrate included two polymers, a hydroxy terminated vinylsiloxane polymer (the linking agent), and a hydrosiloxane polymer for forming cross-links between the polymer strands linking the particles and the surface. The mixture also included the chemical modifying reagent vinyltriacetoxysilane. The polymer strands formed by the linking agent were cross-linked via an addition cross-linking reaction catalysed by a platinum catalyst.

- 35 • The following were mixed together.

0.25g vinylsiloxane polymer (hydroxy terminated) CAS [67923-19-7]

0.25g hydrosiloxane polymer CAS [68037-59-2]

0.36g vinyltriacetoxysilane

CAS [4130-08-9]

1 drop of platinum-divinyltetramethyldisiloxane complex, 3-3.5% platinum concentration

0.12g Aerosil silica powder, and

~ 25 ml of hexane

- The mixture was mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes to disperse the particles and form a uniform mixture. Vibration frequencies of about 40 kHz were used.
- The mixture was removed from the ultrasonic bath.
- Without allowing the mixture to settle, drops of the mixture were deposited onto the surface of the substrate by spray coating.
- The coated substrate was allowed to cure at room temperature for 1-2 days.

The contact angle and hysteresis of water on the coated surface were measured by an automated contact angle instrument goniometer (made by Ramé-hart, Inc) to be:

Glass

Contact angle: 164°

Hysteresis: 18°

Rubber

Contact angle: 151°

Hysteresis: 111°

Example 4

In this example, a hydrophobic coating was applied to the surface of a glass substrate and a rubber substrate as described below. The linking agent was vinylsiloxane polymer (hydroxy terminated). The polymer strands formed by the linking agent were cross-linked via an addition cross-linking reaction catalysed by a platinum catalyst.

- The following were mixed together:

0.25g vinylsiloxane polymer (hydroxy terminated) CAS [67923-19-7]

0.25g hydrosiloxane polymer CAS [68037-59-2]

0.36g methyltriacetoxysilane CAS [4253-34-3]

1 drop of platinum-divinyltetramethyldisiloxane complex, 3-3.5% platinum concentration

0.12g Aerosil silica powder, and

~ 25 ml of hexane

- The mixture was mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes to disperse the particles and form a uniform mixture. Vibration frequencies of about 40 kHz were used.
- 5 • The mixture was removed from the ultrasonic bath.
- Without allowing the mixture to settle, drops of the mixture were deposited onto the surface of the substrate by spray coating.
- The coated substrate was cured at room temperature for 1-2 days.
- 10 The contact angle and hysteresis of water on the coated surfaces were measured by an automated contact angle instrument goniometer (made by Ramé-hart, Inc) to be:

Glass

- Contact angle: 163°
- 15 Hysteresis: 94°

Rubber

- Contact angle: 161°
- 20 Hysteresis: 115°

Example 5

In this example, a hydrophobic coating was applied to a glass substrate and a rubber substrate as described below. The polymer strands were cross-linked via an addition cross-linking reaction catalysed by a platinum catalyst.

- 25 • The following were mixed together:
 - 0.25g vinylbutadiene-siloxane polymer (50% in toluene) CAS [72905-90-9]
 - 0.25g hydrosiloxane polymer CAS [68037-59-2]
 - 0.36g methyltriacetoxysilane CAS [4253-34-3]
 - 30 1 drop of platinum-divinyltetramethyldisiloxane complex, 3-3.5% platinum concentration
 - 0.12g Aerosil silica powder, and
 - ~ 25 ml of hexane
- The mixture was mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes to disperse the particles and form a uniform mixture. Vibration frequencies of about 40 kHz were used.
- 35 • The mixture was removed from the ultrasonic bath.

- Without allowing the mixture to settle, drops of the mixture were deposited onto the surface of the substrate by spray coating.
- The coated substrate was cured at room temperature for 1-2 days.

5 The contact angle and hysteresis of water on the coated surfaces were measured by an automated contact angle instrument goniometer (made by Ramé-hart, Inc) to be:

Glass

Contact angle: 164°
10 Hysteresis: 95°

Rubber

Contact angle: 147°
15 Hysteresis: 112°

The contact angle of water on the coatings prepared in Examples 1 to 5 was similar to the contact angle of water on the coatings prepared in the Comparative Example. Accordingly, the cross-linking of the polymer strands does not have a detrimental effect on the hydrophobicity of the coatings.

20 The method of the invention can be used to prepare hydrophobic coatings on the surface of a variety of solid substrates including metals, alloys, glasses, papers, ceramics, polymers, composites and other materials.

25 The present inventors have found that cross-linking the polymers strands via covalent bonds strengthens the network of chemical bonds in the hydrophobic coating, which enhances the durability of the hydrophobic coating formed by the method of the present invention. The present inventors have surprisingly found that the durability of the hydrophobic coating is enhanced while achieving a similar hydrophobicity to similar
30 hydrophobic coatings in which the polymer strands linking the particles of the particulate material are not cross-linked.

Coatings formed by the method of the present invention have a wide variety of uses. The method of the invention can be used to form coatings on the surfaces of a substrate
35 to inhibit corrosion of the substrate. The method can be used to coat the surface of a substrate to inhibit the formation of crystallisation centres, for example, in water pipelines, closed heat exchanges, tubular boilers, chillers and refrigerators, which use

water, brine solutions, inorganic, alkalies or other electrolytes. The method can also be used to form coatings on surfaces to prevent icing of the surface.

5 The coatings formed by the method of the invention can also be used to provide anti-icing, anti-fouling and anti-corrosion coatings for maritime and other waterways vessels.

10 The coatings can also be used to improve the resistance of surfaces to colonisation by biological organisms such as microflora. The coatings can also be used to provide water resistance or water proofing to surfaces.

The coatings can also be used to reduce drag for water craft.

15 In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprising" and grammatical variations thereof is used in an inclusive sense, i.e. the features specified may be associated with further features in various embodiments of the invention.

CLAIMS:

1. A method of forming a hydrophobic coating on the surface of a substrate, the method comprising the steps of:
 - 5 (a) applying a mixture comprising a particulate material and a linking agent to the surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material;
 - 10 (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands, and
 - 15 (c) exposing the coating to conditions effective to cause at least some of the polymer strands linking two or more particles or linking the surface and one or more particles, to cross-link with other polymer strands linking two or more particles or linking the surface and or one more particles,
 - 20 thereby forming a hydrophobic coating on the surface on which water has a contact angle of at least 130°.
2. A method of forming a hydrophobic coating on the surface of a substrate, the method comprising the steps of:
 - 25 (a) applying a mixture comprising a particulate material, a linking agent and a peroxide, to the surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material, and wherein the peroxide is capable of causing a peroxide catalysed cross-linking reaction between the polymer strands formed by the linking agent;
 - 30 (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles
 - 35

- 5 together and to the surface by polymer strands, and
(c) exposing the coating to conditions effective to cause a peroxide
catalysed cross-linking reaction between at least some of the polymer
strands linking two or more particles or linking the surface and one or
more particles,
thereby forming a hydrophobic coating on the surface on which water has a contact
angle of at least 130°.
- 10 3. A method according to claim 2 wherein the peroxide is selected from dicumyl
peroxide, 2,4-dichlorobenzoyl peroxide, benzoyl peroxide, or a mixture thereof.
- 15 4. A method of forming a hydrophobic coating on the surface of a substrate, the
method comprising the steps of:
(a) applying a mixture comprising a particulate material, a linking agent
and a platinum catalyst, to the surface to form a coating on the surface,
wherein the linking agent is capable of forming a polymer strand
linking two or more particles of the particulate material and capable of
forming a polymer strand linking the surface and one or more particles
of the particulate material, and wherein the platinum catalyst is capable
of catalysing a cross-linking reaction between the polymer strands
formed by the linking agent;
20 (b) exposing the coating to conditions such that the linking agent forms
polymer strands linking two or more particles of the particulate
material, and forms polymer strands linking the surface and one or
more particles of the particulate material, thereby linking the particles
together and to the surface by polymer strands, and
25 (c) exposing the coating to conditions effective to cause a platinum
catalysed cross-linking reaction between at least some of the polymer
strands linking two or more particles or linking the surface and one or
more particles,
30 thereby forming a hydrophobic coating on the surface on which water has a contact
angle of at least 130°.
- 35 5. A method of forming a hydrophobic coating on the surface of a substrate, the
method comprising the steps of:
(a) applying a mixture comprising a particulate material, a linking agent, a
polymer having terminal vinyl groups and a platinum catalyst, to the

5 surface to form a coating on the surface, wherein the linking agent is capable of forming a polymer strand linking two or more particles of the particulate material and capable of forming a polymer strand linking the surface and one or more particles of the particulate material, and wherein the platinum catalyst is capable of catalysing a vinyl addition cross-linking reaction between the polymer having terminated vinyl groups and the polymer strands formed by the linking agent;

10 (b) exposing the coating to conditions such that the linking agent forms polymer strands linking two or more particles of the particulate material, and forms polymer strands linking the surface and one or more particles of the particulate material, thereby linking the particles together and to the surface by polymer strands, and

15 (c) exposing the coating to conditions effective to cause a vinyl addition cross-linking reaction between the polymer having terminal vinyl groups and the polymer strands linking two or more particles or linking the surface and one or more particles,

thereby forming a hydrophobic coating on the surface on which water has a contact angle of at least 130°.

20 6. A method according to claim 5 wherein the polymer having terminal vinyl groups is selected from the group consisting of vinyl terminated polydimethylsiloxane, vinyl terminated diphenylsiloxane-dimethylsiloxane copolymer, vinyl terminated trifluoropropylmethylsiloxane-dimethylsiloxane copolymer and vinylmethyloxysiloxane homopolymer.

25 7. A method according to any one of claims 4 to 6 wherein the platinum catalyst is selected from the group consisting of platinum divinyl complexes and platinum cyclovinyl complexes.

30 8. A method according to any one claims 1 to 7 wherein the linking agent is a polymer or mixture of polymers selected from the group consisting of hydroxy terminated vinylsiloxane polymer, hydroxy terminated polydimethylsiloxane, hydroxy terminated polydiphenylsiloxane, hydroxy terminated polyphenylmethylsiloxane, methylhydrosiloxane (and copolymers with dimethylsiloxane), vinylmethoxysiloxane homopolymer,

35 polytrifluoropropylmethylsiloxane (silanol terminated), vinylmethylsiloxane-dimethylsiloxane copolymer (silanol terminated) and vinylmethylsiloxanes.

9. A method according to any one of claims 1 to 3 wherein the linking agent is a polymer or mixture of polymers selected from the group consisting of modified polystyrene, polyethylenes, fluorinated polymers, and triethoxysilyl modified poly-1,2-butadiene.
10. A method according any one of claims 1 to 9 wherein the mixture at step (a) further comprises a chemical modifying reagent capable of reacting with at least some of the particles of the particulate material to enhance the chemical hydrophobicity of the particles.
11. A method according to claim 10 wherein the chemical modifying reagent is a compound containing one or more condensation cure groups and one or more hydrophobic groups.
12. A method according to claim 11 wherein the chemical modifying reagent is a compound of the formula $\text{SiR}(\text{OAc})_3$, where R is an alkyl group, vinyl or trifluoropropyl, and Ac is an acetyl group.
13. A method according to any one of claims 1 to 12 wherein the particulate material comprises silica particles.
14. A method according to claim 13 wherein the silica particles are flame hydrolysed silica particles.
15. A method accordingly to any one of claims 1 to 12 wherein the particulate material comprises metal particles, glass particles or particles of a metal oxide.
16. A method according to claim 15 wherein the metal oxide is titanium oxide, aluminium oxide, aluminium oxide, zirconium oxide or zinc oxide.
17. A method according to any one of claims 1 to 16 wherein the particles of the particulate material have an average particle size of from 1 nm to 500 μm .
18. A method according to claim 17 wherein the particles of the particulate material have an average particle size in the range of from 1 nm to 100 μm .
19. A method according to claim 19 wherein the particles of the particulate material

have an average particle size in the range of from 1 nm to 50 nm.

- 5 20. A method according to any one of claims 1 to 19 wherein step (b) involves heating the coating to a temperature and for a time effective for the linking agent to form polymer strands linking two or more particles of the particulate material, and polymer strands linking the surface and one or more particles of the particulate material.
- 10 21. A method according to any one of claims 1 to 20 wherein step (c) involves heating the coating to a temperature of up to 150 °C for a time effective to cause the polymer strands to cross-link.
- 15 22. A method according to any one of claims 1 to 21 wherein steps (b) and (c) are carried out simultaneously.
- 20 23. A method according to any one of claims 1 to 21 wherein step (b) is carried out prior to step (c).
- 25 24. A method according to any one of claims 1 to 23 wherein the contact angle of water on the coating formed by the method is at least 150°.
- 25 25. A method according to any one of claims 1 to 24 wherein the contact angle of water on the coating formed by the method is at least 160°.
- 30 26. A coating produced by the method according to any one of claims 1 to 25.
- 35 27. An object having a surface at least a portion of which is coated with a hydrophobic coating formed by the method according to any one of claims 1 to 25.

Dated this 11th day of April 2003

UNISEARCH LIMITED

By their Patent Attorneys

GRIFFITH HACK

This Page is inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images
problems checked, please do not report the
problems to the IFW Image Problem Mailbox**